



Utilization of Bis(salicylaldehyde)orthophenylenediamine for the Separation of Gold and Chromium by Capillary Zone Electrophoresis

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Abstract

BSOPD, bis(salicylaldehyde) orthophenylenediamine) is investigated as complexing agent in capillary electrophoresis for determination of gold and chromium. BSOPD was chosen as the UV-Visible absorbing chelating ligand because of its ability to form stable complexes with metal ions. Both the metal ions can be determined in single run under optimized conditions with run time of 12 minutes including coexisted ions usually present in waste water. Separation was achieved at optimized conditions of 50 mM phosphate buffer as a background electrolyte at pH =3.4, at applied voltage of -10 kV and detection wavelength of 231 nm. Under above mentioned conditions, limit of quantification (0.5 and 10 $\mu\text{g mL}^{-1}$) and detection limit (0.1667 and 3.33 $\mu\text{g mL}^{-1}$) were found for Au(III) and Cr(VI), respectively. Linear calibration graphs were obtained 0.5 – 50 $\mu\text{g mL}^{-1}$ for Au(III) and 10 – 60 $\mu\text{g mL}^{-1}$ for Cr(VI) with the correlation coefficient value 0.996 and 0.993, respectively. Utility of this method for metal analysis has been investigated by determining gold from wastewater samples of goldsmith factories and chromium in some environmental waters (portable and polluted).The method was validated by comparing results obtained with capillary zone electrophoresis with atomic absorption spectroscopy.

Keywords: Bis(salicylaldehyde)orthophenylenediamine (BSOPD), Separation of gold and chromium, CZE.

Introduction

Capillary electrophoresis is one of the most powerful techniques used to simultaneously separate and determine inorganic ions. It yields highly efficient separation, good repeatability, simple operation and rapid detection, along with very low consumption of electrolyte and sample [1, 2]. One of the problems using CE for the separation of cation has a similar mobility, resulting in poor resolution. However, complexation of cations with a ligand to form charged complexes can be used to modify the mobility of cation as each cation will complex with ligand to a different degree determined by the complex stability [3]. This approach allows for

direct UV detection of metal ions after chelating with suitable UV absorbing ligand [3].BSOPD which is one of the most popular symmetrical tetradentate ligands, forms complexes with various metal ions and organic compounds [4]. The study of complexation reaction of this ligand in aqueous and nonaqueous matrices could be used as an efficient strategy to design the analytical systems such as, bulk liquid membrane[5], solid-phase extraction [6-9], catalyst [10,11], sensors[12-19] and biochemistry [20,21]. BSOPD related complexing agents have also found applications as spectrophotometric derivatizing reagents for metal ions in CE and HPLC [22, 23]. Selectivity of

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analysis depends on pH and reaction conditions. BSOPD itself is reported to form stable complexes with gold [24], chromium [25] and cobalt [26] have been utilized for their spectrophotometric determination.

Gold belongs to the element that occurs on the earth with very low natural contents. It is one of the most important noble metal due to its wide applications in industry and economic activity. For this reason, a simple, sensitive and selective method for determination of trace gold is required strongly [27]. Chromium is a major pollutant for environment, Cr(VI) is carcinogen because of its unique biochemical role [28]. The separation, preconcentration and determination process of trace metal ions from different matrices especially in water samples are mainly based on the utilization and application of a number of available techniques [29]. These includes UV-Visible, atomic absorption spectroscopy (AAS), high performance liquid chromatography (HPLC) and voltammetry [30 – 33]. Keeping in view of the simplicity of CE based assay procedures; BSOPD has been investigated for its utility as complexing agent for gold and chromium in capillary zone electrophoretic conditions.

To the best of our literature survey, there is no previous reported work on the use of BSOPD for the separation and determination of these two metal cations; Au(III) and Cr(VI) by capillary zone electrophoresis.

Experimental

Reagents and instrumentation

All reagent used were of analytical or equivalent grade and were obtained from Fluka (Switzerland) and Merck (Germany). The reagent BSOPD was synthesized according to report [33]. The solution was prepared by dissolving the requisite amount of BSOPD in a known volume of double distilled ethanol (Merck, Darmstadt). More dilute solution of the reagent was prepared as required. Appropriate amounts of metal salts gold chloride and potassium dichromate were dissolved to make stock standard solution of 1000 mg L⁻¹. Buffer solution pH 1-10 at unit interval were prepared as: hydrochloric acid (0.1M) and potassium chloride (0.1M) pH 1-2; acetic acid (0.1M) and sodium acetate (0.1M) pH 3-6; boric

acid (0.1M) and sodium tetraborate (0.1M) pH 8-9; sodium bicarbonate, sodium carbonate pH 10 and phosphoric acid (0.1M) and sodium dihydrogen phosphate(0.1M) pH 2-7. The wastewater samples were obtained from common tannery treatment plant of tannery complex and goldsmith factories (Karachi, Pakistan).

The CE system consists of Beckman Coulter P/ACE MDQ, USA equipped with photodiode array detector and MDQ 32 Karat software was used. Uncoated fused silica capillaries of 60 cm total length, 54 cm effective length and 75µm i.d were obtained from Beckman Instruments. The temperature of capillary and samples were maintained at 25°C. Prior to sample run, the capillary was regenerated and conditioned as reported [34]. The sample was injected by an auto sampler with a pressure of 0.5 psi.

Analytical procedure

Aqueous solution containing 25 µg mL⁻¹ of gold and 50 µg mL⁻¹ amounts of chromium was transferred to 10 mL volumetric flask, and 4 mL of reagent (0.05% w/v solution in ethanol) and running buffer was added. The mixture was diluted to the mark with de-ionized water. Finally an aliquot of complex was transferred to the CE tube and electropherogram was recorded as shown in (Fig.1). The similar complexation method was used to study spectrophotometric condition for optimization by UV-Visible spectrophotometer.

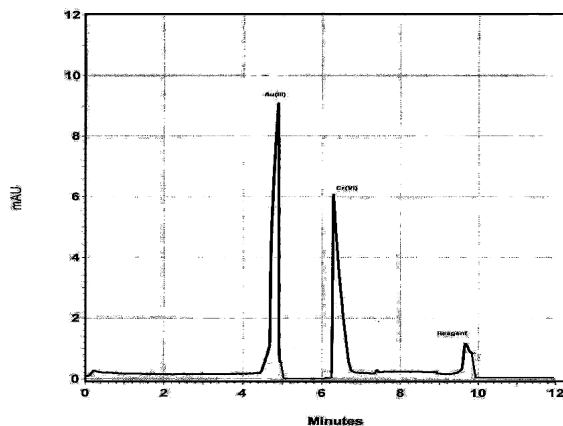


Figure 1. Separation of Au(III) and Cr(VI), 50mM phosphate buffer at pH 3.4 and injection time of 0.4 s, applied voltage of -10kV, and reagent concentration of 4 ml of 1.37mM.

Determination of gold (III) in certified reference materials (SH24)

A 25 g sample was accurately weighed and dissolved in aqua regia and placed in a 250 ml round bottom flask and it was refluxed for 6 h. The contents of the flask were transferred to 25-mL volumetric flask and warmed up to dryness then made up to 25 mL volume with de-ionized water. The quantitation of this solution was carried out with the external calibration curve prepared from the standard solution of Au(III) using the same method described as above.

Determination of gold in wastewater (goldsmith factories) sample

An aliquot (1 – 2 mL) of filtered (with Whatman No. 42) wastewater sample was pipetted into a 10-mL calibrated flask, and the gold content was determined with the external calibration curve prepared from the standard solution using the same proposed method. The wastewater sample was collected from goldsmith factory (Karachi, Pakistan).

Determination of chromium in wastewater from industrial effluent sample

Filtered (with Whatman No. 42) wastewater sample (100 mL) was evaporated upto 15 mL. The resulting solution was then filtered and volume was made up to 150 mL with de-ionized water. The effluent from the common tannery treatment plant of tannery complex, Karachi was taken and diluted as per requirement.

An aliquot (1 – 2 mL) of this solution was pipetted into a 10-mL calibrated flask, and the chromium content was determined with the external calibration curve prepared from the standard solution using as describe under procedure.

Results and Discussions

Pre-column derivatization conditions

It was found that Au(III) and Cr(VI) could form sensitive color complexes with BSOPD in a weak acidic environment. The effect of pH on the chelating reaction, metal to ligand ratio, molar

absorptivity and stability of metal ion complexes were investigated by spectrophotometric method (Table 1) (Fig. 2). It could be found that the absorption maxima of metal complexes in visible region is little different, however another band in UV region at 231 nm can be used for simultaneous detection of gold and chromium in single run. Also, shorter wavelength bands are intense and pronounce at low concentrations which are the case in the CE detection, hence detection wavelength of 231 nm was selected for further studies.

Table 1. Quantitative spectrophotometric data of color reaction of BSOPD with metal ions.

Metal ions	pH of Max Absorbance	Metal: Ligand ratio	λ_{max} nm	$\epsilon=10^4$ Lmol ⁻¹ cm ⁻¹	Solution Stability/Temp.
Au(III)	3	1:1	450	32.59	24 hr (25 ± 5°C)
Cr(VI)	4	1:4	440	2.25	24 hr (25 ± 5°C)

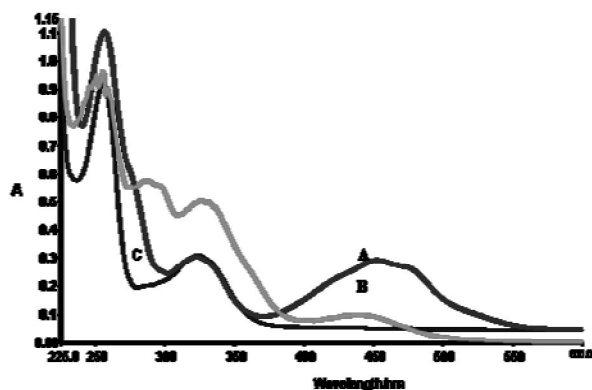


Figure 2. A, B and C absorption spectra of Au(III) - BSOPD, Cr(VI) - BSOPD system and the reagent blank at (λ_{max} = 231nm).

Selection of separation conditions

At the start of the work, certain conditions [35] of buffer concentration (50mM phosphate electrolyte), buffer pH (3.4) and voltage applied (-10 kV) were used for the analytical run of the standards for cations under study keeping the capillary voltage at 25 °C. Each of these condition was then systematically adjusted, with the others remaining unchanged, in order to establish variation data for each parameter. The sample was introduced by hydrostatic mode injection.

Effect of type and pH of background system

The type of electrolyte played an important role in CE separations. We studied the effects of three electrolytes on the separation, including sodium acetate-acetic acid (NaAc-HAc), Boric acid- sodium borate and phosphoric acid-sodium phosphate. Metal complexes did not show any migration in NaAc-HAc buffer system where as good peaks were observed with borate, but both complexes have similar mobility in borate buffer therefore no separation could be achieved using this buffer along with various surfactants [nonionic {polyoxyethylene -octylphenyl ether (TritonX-100)}; cationic {cetyltrimethylammonium bromide (CTAB)}; and anionic {sodium dodecyl sulfate (SDS)}], and organic modifiers (Acetonitril, methanol, butanol, 1-pentanol). Phosphate buffer showed preferable separation, better selectivity, high reproducibility, and sharp peaks. Therefore, different concentrations of phosphate buffer in range of 12.5 – 80 mM have been optimized and 50 mM phosphate at pH 3.4 was found to have better separation and has been selected as run buffer.

Effect of electrolyte pH on migration time (t_m)

It is possible to consider pH as one of the most important separation parameters in CZE since it affects the net charge of the cations and also the electro-osmotic flow (EOF)[35] consequently movement of analyte species is affected by pH. In the experimental, the effect of pH on the sensitivity and separation was studied in the range of pH 2.00-7.00 (Fig. 3.)

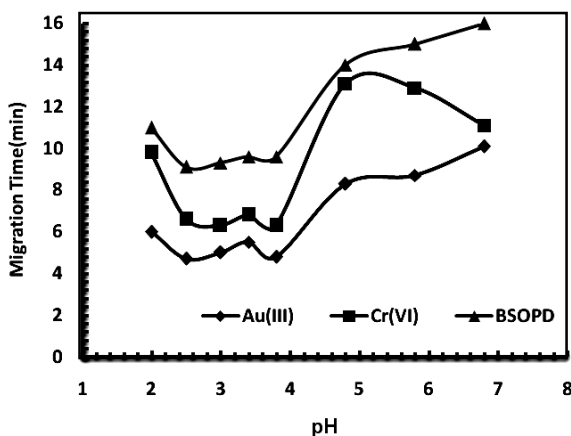


Figure 3. Effect of pH on migration time.

If the pH was less than 2.5 or more than 6, poor separation between Au(III) and Cr(VI) or long run times were observed. As shown in figure both metal ions can be separated including reagent in the range of pH 2.5- 4.00, however, at pH 3.4 good separation was possible with shorter run time hence selected for further studies.

Influence/effect of voltage on migration time (t_m)

Generally, both applied voltage and temperature affect migration time of ions in electrolyte. Increasing the applied voltage, the migration time of ions shortens; the higher temperature could also cause the migration time to be short. That is to say, under higher voltage and temperature the speed of ions would be faster. However, high voltage can cause the Joule-heat formed to raise temperature, and higher temperature gives a bad repeatability [36]. From the voltage settings (-5) – (-20) kV; the adopted applied voltage is -10kV at 25°C. (Fig. 4) shows baseline separation of both cations Au(III) and Cr(VI) within 12 min.

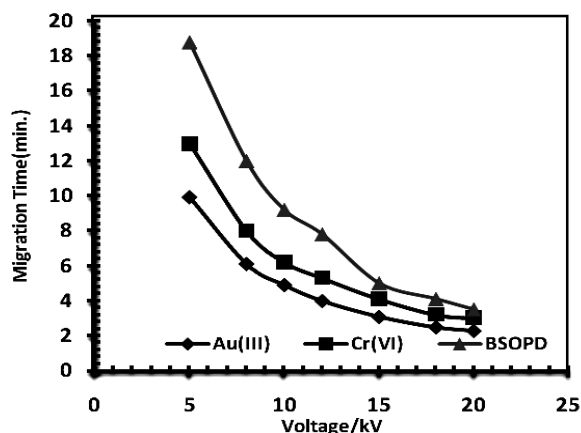


Figure 4. Effect of voltage on migration time.

Influence/effect of electrolyte concentration on migration time (t_m)

Control of electrolyte concentration is a tool that should be kept in mind as tool in improving efficiency, sensitivity and resolution [37]. Different Concentrations (12.5 – 80 mM) of phosphate were optimized at pH = 3.4. As seen in (Fig. 5) at every instance the t_m values are more or less same by increasing concentrations of

phosphate buffer but the best resolutions were obtained at the intermediate concentrations within the range studied with the data obtained, it was decided the most suitable concentration for our purposes is 50 mM, as it yields the best resolution. All results of optimizations are summarized in (Table 2).

Table 2. CE parameters obtained with optimization experiments.

Parameters	Studied range	Selected value
Wavelength (λ_{max}) / nm	231,250,301,310	231
pH of running buffer 50mM (Phosphate)	2- 7	3.4
Applied Pressure for sample injection/Psi		0.5
Injection time of sample/sec	0.4 - 10	0.4
Length / cm x I.D		50 cm bare silica capillary (id.75 μ m)
Applied Voltage / kV	-5 – (-20)	-10
Concentration of reagent (mM)	0.137 – 0.959	0.548

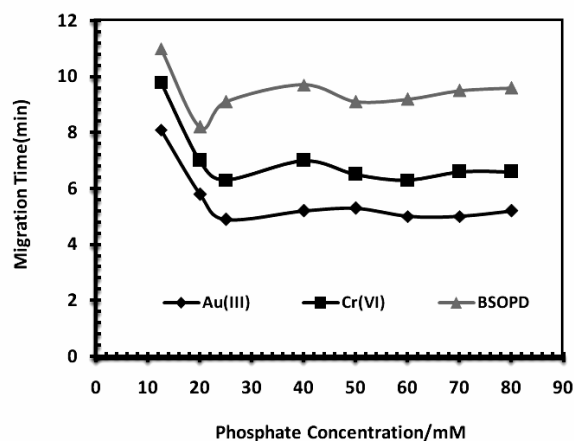


Figure 5. Effect buffer concentration on migration time.

Quantification

Under optimized as mentioned above, calibration curves of these two metal ions were constructed from five calibration levels by plotting peak heights versus concentrations. Detection limits were calculated based on a peak height of thrice the baseline noise while limits of quantification were calculated as 10 times of baseline noise. Results for analytical figures of merit are given in (Table 3).

Table 3. Quantitative data of metal chelates of BSOPD Complexes by CZE.

Metal ion	Calibration range ($\mu\text{g mL}^{-1}$)	Limit of quantification ($\mu\text{g mL}^{-1}$)	Limit of detection (LOD) ($\mu\text{g mL}^{-1}$)	Coefficient of Determination R^2	Linear regression equation
Au(III)	0.5-50	0.5	0.167	0.996	$y=0.553x + 0.491$
Cr(VI)	10-60	10	3.333	0.993	$y= 0.142x - 1.102$

Effect of associated ions

Effect of some commonly associated metal ions has been investigated at optimized conditions. No significant interferences were found from Cr(III), Cu, Co, Fe, Ni, Pt, and Ag. Although BSOPD form complexes with Co and Cr(III), no peaks were detected, due to insolubility of chromium(III) and cobalt complexes in aqueous solution during separation.

Applications

The developed method was applied to certified reference samples (SH24) for gold in order to evaluate the quantitative performance. Method was also used for the determination of gold in wastewater from goldsmith and tannery wastewater sample from industrial effluent. The assay results are listed in Table 4a-4b. Good agreement between values obtained by CE method and the certified value for gold were observed. The results of the wastewater analyses by the proposed method were in good agreement with those of by AAS.

Table 4a. Determination of gold in CRM(SH-24).

Certified Reference material (composition)	Amount present in Certified reference material (CRM)/ $\mu\text{g g}^{-1}$	% recovery	Amount found by CE with Internal standard addition $\mu\text{g g}^{-1}$ RSD (%) (n=3)
SH-24 (SiO_2 , Al_2O_3 , Na_2O , K_2O , CaO , MgO , TiO_2 , MnO , P_2O_5 , Fe, S)	1.326	91.25%	1.21(0.415)

Table 4b. Determination of gold and chromium in wastewater.

Sample	Amount found by CE With calibration in $\mu\text{g mL}^{-1}$ RSD (%) (n=3)	Amount found by AAS $\mu\text{g mL}^{-1}$
$^1\text{Au(III)}$	0.378(2.02)	0.341
$^2\text{Cr(VI)}$	0.032(0.134)	0.032

Conclusions

This paper demonstrates the separation and determination of gold and chromium, as their BSOPD – complex by CE. BSOPD can form water soluble complexes with these two metals ions in mixed system hence the hazardous extraction steps can be avoided. Metal ion determination by CE can be proposed as inexpensive alternative at $\mu\text{g mL}^{-1}$ levels. Results of the determination of gold from CRM sample showed that the method can reliably be applied to real systems.

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